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Unique Place of the Milk Proteins

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Casein is the main protein in milk. It constitutes about 3 percent of average cow's milk. Other proteins are present in smaller amounts. Often they are considered not as individual substances, but altogether as whey proteins or heat-coagulable proteins of whey.

Because of the properties peculiar to the casein molecule that make it useful for many purposes and because of the ease with which this protein can be prepared from skim milk in relatively pure form, casein has occupied a unique position in industry. We use approximately 60 million pounds of it for industrial purposes each year—approximately 55 percent in paper making, 15 percent for adhesives, 10 percent for paints, 5 percent for plastics, and 15 percent for other purposes.

The casein in skim milk is in the form of its calcium salt in colloidal solution. On the addition of acid, the calcium is displaced and the casein precipitates as a curd. Alternatively, rennet may be added to skim milk to precipitate casein. Both methods are used in the manufacture of casein for industrial purposes. In the United States, the acid-precipitation method is used almost exclusively, because it gives a product suitable for most uses. Rennet casein, because of special properties, is preferred for the manufacture of plastics. It is largely imported, particularly from Argentina.

The first step in making acid-precipitated casein is acidification. Hydrochloric acid or sulfuric acid is added to the skim milk or the milk is allowed to sour, in which case lactic acid, produced by fermentation of lactose, is the effective precipitant. The precipitated curd is then drained, washed, pressed to remove water, milled, dried, and ground.

Rennet casein is precipitated from skim milk by the action of the enzyme rennin, instead of by acidification. Thereafter, the method of manufacture is the same as the acid-precipitation method.

THE BINDING strength and adhesive powers of casein solutions give this protein wide use in the preparation of coated papers. Such papers (also called glazed, enameled, or art papers) are used for lithographic work and for printing books, magazines, and advertisements. Coated papers are made by applying to the paper in a thin, even layer a mixture of mineral substances (clays, blanc fixe, chalks) suspended in a solution of casein. The coating covers the individual fibers on the surface of the paper and fills any hollows between them, so that the paper will have smooth, semiabsorbent surfaces after calendering or polishing. The casein binds the finely divided mineral matter to the paper so that it will not be picked off during printing; the mineral substances form a surface which is receptive to ink. Casein also is used, though to a lesser extent, in the manufacture of washable wallpapers, box papers, water-resistant papers, and playing cards.

Solutions of casein in alkalies (with enough of the protein to give a suitable viscosity) can be used as glue. Such a glue compares favorably in strength with animal glue, but it is not water-resistant. Resistance to water can be imparted to casein glue, however, by modifying the simple formula of casein in alkali; these improved casein glues are widely useful in industry. Prepared casein glues are sold in the form of dry mixtures, which need only the addition of water before use. They are commonly composed of casein, lime, and a number of alkaline salts. Various chemicals have been used to improve the resistance to water, and many colloidal materials with adhesive properties can be mixed with casein to modify the properties of the resulting glues. It has thus been possible to adapt casein glues to a variety of specialized applications. These glues are used in the woodworking industry, in gluing paper, and in many other fields.

The use of casein as a vehicle, or binder, for paint dates from ancient times. Modern casein paints consist essentially of aqueous alkaline solutions of casein plus suitable pigments.

Marketed either as a dry powder or as a soft paste, casein paint mixtures require only the addition of water before application. Newer paints of this type—that is, paints to be thinned with water—are emulsion paints in which the liquid portion is an oil-in-water emulsion and casein is the emulsifying agent that prevents separation of the liquid phases. Each of these paints—dry powder casein paint, paste casein paint, and oil-containing casein paint—has certain advantages, and all are used extensively. In both cost and utility, casein paints stand between calcimines and flat wall paints.

GROUND CASEIN can be converted into fibrous forms by extruding an alkaline solution of the protein into an acid coagulating bath, or by extruding a heated mixture of casein and water into air. The term "casein fiber" is reserved for the fine filaments obtained by the first method. The coarser product of the second method is called casein bristle.

To make casein bristles, a heated mixture of casein and water is extruded through a suitable die and the filaments, as they emerge into the air, are stretched and hardened under tension with quinone or formaldehyde, after which they are washed and dried. At first, the process was a batch process, but it has since been developed into a continuous process. The finished casein bristles are cylindrical. If they are hardened with quinone they are black. The stiffness of the bristle varies with the diameter. Bristles with a diameter of 0.024 inch are extremely stiff, but those with a diameter of 0.008 inch are soft and pliable. Brushes of different types have been made with the material, which seems particularly suitable for paint brushes. Such paint brushes, although made of untapered bristle, have good paint-carrying capacity, leave smooth films, and wear well. The bristles are resistant to oil and fat solvents, but soften when allowed to stand in water.

THE CASEIN PLASTICS industry uses a great deal of casein, but in the United States it is a smaller industry than in Europe before the war.

To make casein plastics, a finely ground, high-grade rennet casein is mixed well with 20 to 30 percent of water. Dyes, pigments, and other chemicals may also be added during the mixing operation. The mixture, still in the form of a powder, is converted by extruding machines into soft plastic, usually in the form of long rods. Sheet material may be prepared from the soft plastic by pressure, heat, and the use of sheet frames of the desired size. The rods or sheets are then soaked in formaldehyde until thoroughly hardened, or they may first be cut into small objects or blanks and then hardened. In either instance, the hardening process is laborious and slow. The hardened product is washed and dried.

Because of the relatively high water absorption of casein and the dimensional instability of casein plastics, the plastics are not used for large objects. They are of particular value for making buttons, buckles, beads, and costume jewelry. The beautiful colors and lustrous finish that can be given casein plastics are largely responsible for the continuing usefulness of casein in this field.

Research on the improvement of casein plastics continues in the Department of Agriculture. A primary objective has been to convert casein by chemical modification into derivatives that could be molded by compression directly into finished articles with improved resistance to water. Some success has been achieved. Derivatives of various types were prepared; some of them can be molded directly into small finished articles, and the time-consuming commercial process thus avoided. The water absorption of the plastics has been reduced. The successful processes of modification, however, have not been cheap, and their commercial development is perhaps unlikely.

Casein is put to many uses in which its adhesive or emulsifying qualities are valuable. These include: In pigment finishes and seasonings in the leather industry; in finishing and sizing operations in the textile industry; as a spreader, sticker, and emulsifier in insecticides; as an emulsifying agent in emulsion polymerization of synthetic rubber; as an adhesive for rayon cord in rubber tires; and as a binder in printing inks. It is used also as a raw material for the production of protein hydrolyzates of high biological value.

THE PROTEINS (only 0.6 percent) in whey represent another possible source of industrial protein. At present they are not separated from whey in large quantities. Limited amounts are prepared as heat-coagulated protein, which is incorporated into feeds or converted to amino acid mixtures of excellent nutritive quality.

Heat-coagulated whey protein, however, cannot be considered a typical industrial protein, for the process of coagulation by heat destroys most of the useful properties of the original protein. Because some 50 million pounds of protein occur in whey, which is either wasted or used in stock feeds, attempts have been made to develop methods whereby this potentially useful protein could be prepared in essentially unaltered form.

One approach to the problem has been to search for a precipitant that would effect separation of unaltered protein from the water, lactose, and minor constituents of whey. For example, when I was conducting research for a commercial laboratory, I suggested the use of hexametaphosphoric acid in this connection. Hexametaphosphoric acid, a complex form of phosphoric acid, combines with whey protein to yield an insoluble compound from which water-soluble whey protein can be regenerated.

In a different approach to the problem, A. Leviton, of the Bureau of Dairy Industry, has used dried whey for the preparation of soluble whey protein. According to his method, the lactose in dried whey is extracted with alcohol, which leaves residual whey protein in water-soluble form. None of the proposed methods has found commercial application; probably more efficient utilization of whey protein will depend on the discovery of some cheaper method for separating the material in a commercially useful form.

Skim milk, produced from the separation of butter and cream to the extent of about 50 billion pounds a year, is a cheap and abundant raw material for casein manufacture. Such developments as casein bristle will provide new markets for the protein and will aid in the more effective utilization of skim milk.

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